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Dr. Kenneth J. Wynne

6. AUTHOR(S)

Ke Yang, X. Wang, W. Kim, A. Jain, L. Li, J. Kumar, S. Tripathy,

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

University of Massachusetts Lowell
Department of Chemistry
1 University Avenue
Lowell, MA 01854

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Ke Yang, X. Wang, W. Kim, A. Jain, L. Li, J. Kumar, S. Tripathy,

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University of Massachusetts Lowell
Department of Chemistry
Lowell, Massachusetts

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CHARACTERIZING THE NLO CHROMOPHORE ORIENTATION OF POLYMERIC FILM BY ELECTROABSORPTION SPECTROSCOPY

Ke Yang *, Xiaogong Wang **, Woohong Kim ***, Aloke Jain *, Lian Li *, Jayant Kumar * and Sukant Tripathy **,
*Departments of Physics and **Department of Chemistry, Center for Advanced Materials, University of Massachusetts Lowell, Lowell, MA 01854, U. S. A..
***Samsung Central Research Institute of Chemical Technology, Taejon, Korea 305-380.

Abstract

The dispersion of third-order nonlinear coefficients $\chi^{(3)}_{1133}$ and $\chi^{(3)}_{3333}$ of three different NLO(nonlinear optical) polymer films were determined by electroabsorption spectroscopy. The first material investigated is an epoxy-based polymer BP-2A-NT, with azobenzene NLO chromophore 4-[((4-nitrophenyl)(azo)phenyl)azo)]aniline in its side chain. The other materials are two polydiacetylenes, poly(BPOD) and poly(4-BCMU), in which the delocalized polymer chains contribute to the third-order nonlinearity. The complex spectrum of $\chi^{(3)}_{3333}$ of each material is very similar in shape to corresponding $\chi^{(3)}_{1133}$ spectrum. The ratio of $\chi^{(3)}_{3333}$ to $\chi^{(3)}_{1133}$ is 3.2 for BP-2A-NT, 1.5 for both poly(BPOD) and poly(4-BCMU). These ratios indicate that the distribution of the side-chain NLO chromophores of BP-2A-NT is very close to three-dimensional isotropy, and the distribution of the main-chain chromophores of poly(BPOD) and poly(4-BCMU) is concentrated on the film plane.

I. Introduction

Nonlinear optical (NLO) polymers have received a great deal of attention as promising electro-optic materials over the past decade[1-3]. Various of NLO polymers have been developed as candidate materials for application in high frequency optical modulators and integrated semiconductor-NLO polymer circuits[4-7]. Among these applications, not only the nonlinearity of the material, but also the orientation of the NLO chromophore is of great concern, since a practical application needs to employ a particular or a combination of NLO tensor elements which are sensitive to the orientation of the NLO chromophores.

Electroabsorption spectroscopy can determine the dispersion of each $\chi^{(3)}$ component and can provide information about chromophore orientation in the material[8-10]. The normal incidence of electroabsorption can determine the imaginary part of the change of refractive index $\delta\kappa$ which is due to the applied electric field and is associated with the component $\chi^{(3)}_{1133}$. By using Kramers-Kronig relation , the real part of the change of the refractive index δn can be determined. The complex value of $\chi^{(3)}_{1133}$ is subsequently determined. Similarly, electroabsorption at tilted incidence can determine the complex value $\chi^{(3)'}_{eff}$, which is composed of $\chi^{(3)}_{1133}$ and $\chi^{(3)}_{3333}$. Thus $\chi^{(3)}_{3333}$ can be uniquely determined from these measurements. The obtained ratio of $\chi^{(3)}_{3333}$ to $\chi^{(3)}_{1133}$ can be utilized to offer information about the arrangement of the chromophores which can be treated as a microscopic one-dimensional rod like unit. If the ratio of $\chi^{(3)}_{3333}$ to $\chi^{(3)}_{1133}$ is less than 3, the chromophores are inclined to lie along the film plane. If the ratio of $\chi^{(3)}_{3333}$ to $\chi^{(3)}_{1133}$ equals 3, the chromophores are isotropically oriented in three-dimensional space. If the ratio of $\chi^{(3)}_{3333}$ to $\chi^{(3)}_{1133}$ is larger than 3, the chromophores are inclined to maintain perpendicular to the film plane.

In this paper, we apply this technique to two polydiacetylenes with main-chain chromophore[11], and an epoxy-based polymer BP-2A-NT[12], with side-chain chromophore, to study their third-order nonlinearity and chromophore orientation. Figure 1 shows their molecular structures.

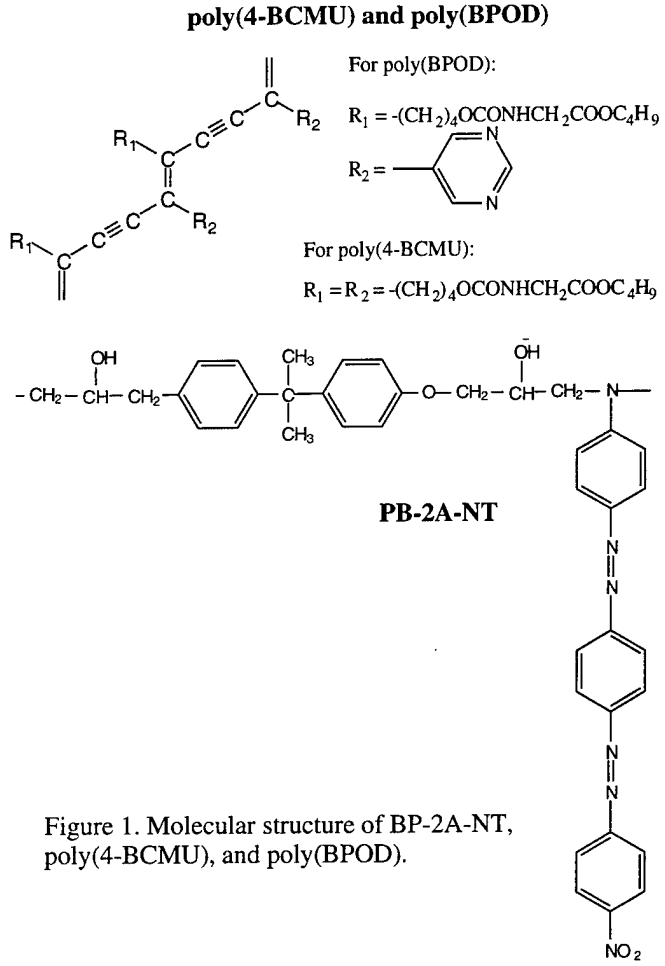

Figure 1. Molecular structure of BP-2A-NT, poly(4-BCMU), and poly(BPOD).

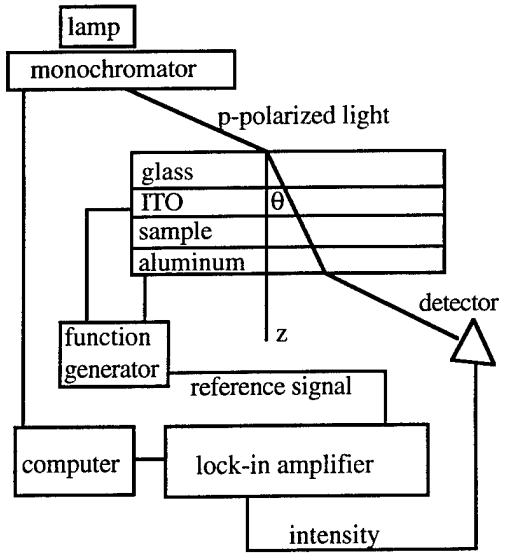

Figure 2. Experimental setup of electroabsorption.

II. Experimental

A layer of 2330 Å poly(BPOD) was spin coated on an indium tin oxide(ITO)-glass substrate. A layer of aluminum film (~220 Å) was deposited as the top electrode on the poly(BPOD) film after thorough drying. A sinusoidal electric field ($E_{ac} = E_{aco}\cos\Omega t$, $\Omega = 2\pi f$, f = 1KHz, $V_{p\text{-}p}$ = 25.5 V) was applied to the sample. A beam of p-polarized light coming from a tungsten lamp through a monochromator was incident on the sample with the angles of 53° and 0° ($\theta_0 = 0°$ for normal incidence). The electroabsorption signal $\Delta I_{2\Omega}$, which is defined as the change in the output intensity I at twice of the modulation frequency, was detected by the lock-in amplifier in 2f mode. The sign of $\Delta I_{2\Omega}$ was determined by comparing the amplified signal from lock-in amplifier in 2f mode and the reference signal from the function generator on an oscilloscope. A micro computer was used to control the monochromator and record data from the lock-in amplifier. The experimental setup is shown in Figure 2. For poly(4-BCMU), the experimental conditions were the following: poly(4-BCMU) thickness is 3506 Å; aluminum electrode thickness ~ 300 Å; Other experimental conditions were same as for poly(BPOD). For BP-2A-NT, the experimental conditions were the following: BP-2A-NT thickness is 4246 Å, gold electrode thickness ~ 250 Å. Other experimental conditions were same as those for poly(BPOD). The measurement of poly(BPOD) was performed in the wavelength range of 470nm to 730nm with the angle of incidence 0° and 53°. The measurement of poly(4-BCMU) was performed from

wavelength of 400nm to 700nm with the angle of incidence 0° and 52°. The measurement of BP-2A-NT was performed from wavelength of 400nm to 750nm with the angle of incidence 0° and 69° .

The dispersions of the real and imaginary parts of the complex refractive index $\tilde{n} = n + i\kappa$ of poly(BPOD), poly(4-BCMU) and BP-2A-NT were measured by an ellipsometer (Rudolph Research, Type 43603-200E) and a spectrometer (Perkin-Elmer Lambda 9).

III. Data Processing

Let us consider the case of tilted incidence of electroabsorption spectroscopy with p polarization (see Figure 2 for the experimental setup). The expression of $\Delta I_{2\Omega} / I$ is given by reference [8]:

$$\frac{\Delta I_{2\Omega}}{I} = -2\pi \cdot \frac{\omega}{c} t_k E_{aco}^2 \cdot 3\,\mathrm{Im}\left(\frac{\chi_{eff}^{(3)}}{\tilde{n}\cos\theta}\right) \qquad (1)$$

where $\tilde{n}$ is the complex refractive index of the absorptive sample, θ is the complex angle of light propagation inside the material, which is related to the angle of incidence θ_o by Snell's law: $n_o \sin\theta_o = \tilde{n}\sin\theta$ $(n_o = 1)$, t_k is the sample thickness, E_{aco} is the amplitude of the applied electric field. $\chi_{eff}^{(3)}$ is given by:

$$\chi_{eff}^{(3)} = \chi_{1133}^{(3)}\cos^2\theta + \chi_{3333}^{(3)}\sin^2\theta \qquad (2)$$

By measuring $\Delta I_{2\Omega} / I$, we can determine the imaginary part of the complex quantity:

$$\chi_{eff}^{(3)'} = \frac{\chi_{eff}^{(3)}}{\tilde{n}\cos\theta} = \frac{\chi_{1133}^{(3)}\cos^2\theta + \chi_{3333}^{(3)}\sin^2\theta}{\tilde{n}\cos\theta} \qquad (3)$$

Its real part can be obtained from Kramers-Kronig relation:

$$\mathrm{Re}[\chi_{eff}^{(3)'}(\omega)] = \frac{2}{\pi}\int_{\omega_i}^{\omega_f} \frac{\omega'\,d\omega'}{\omega'^2 - \omega^2}\,\mathrm{Im}[\chi_{eff}^{(3)'}(\omega')] \qquad (4)$$

where ω_i and ω_f are initial and final optical frequencies, respectively. The complex variable $\chi_{eff}^{(3)'}$ is thus obtained.

For the normal incidence, $\theta = \theta_o = 0$, then $\chi_{eff}^{(3)'}(\theta = 0) = \frac{1}{\tilde{n}}\chi_{1133}^{(3)}$, and $\chi_{1133}^{(3)}$ is determined. At the tilted incidence , $\chi_{3333}^{(3)}$ is determined from the expression of $\chi_{eff}^{(3)'}$, which gives:

$$\chi_{3333}^{(3)} = \left(\frac{\tilde{n}}{\cos\theta}\chi_{eff}^{(3)'}\Big|_{tilted} - \chi_{1133}^{(3)}\right)\left(\frac{\tilde{n}^2}{\sin^2\theta_0}\Big|_{tilted} - 1\right) \qquad (5)$$

By measuring $\tilde{n} = n + i\kappa$ and determining $\chi_{eff}^{(3)'}$ through electroabsorption spectroscopy and Kramers-Kronig relation, $\chi_{1133}^{(3)}$ and $\chi_{3333}^{(3)}$ could be determined independently (without using the relation $\chi_{3333}^{(3)} = 3\chi_{1133}^{(3)}$).

IV. Results and Discussion

The dispersions of $\chi_{1133}^{(3)}$ and $\chi_{3333}^{(3)}$ of these material are shown in Figure 3 to 8. We can see that the shape of $\chi_{3333}^{(3)}$ is similar to that of $\chi_{1133}^{(3)}$ for these materials. Their ratio were found to be $\chi_{3333}^{(3)}:\chi_{1133}^{(3)} \approx 1.5$ for both poly (BPOD) and poly(BCMU), $\chi_{3333}^{(3)}:\chi_{1133}^{(3)} \approx 3.2$ for BP-2A-NT. Their chromophores (i.e. the side chain of BP-2A-NT or the main-chain segment of the two

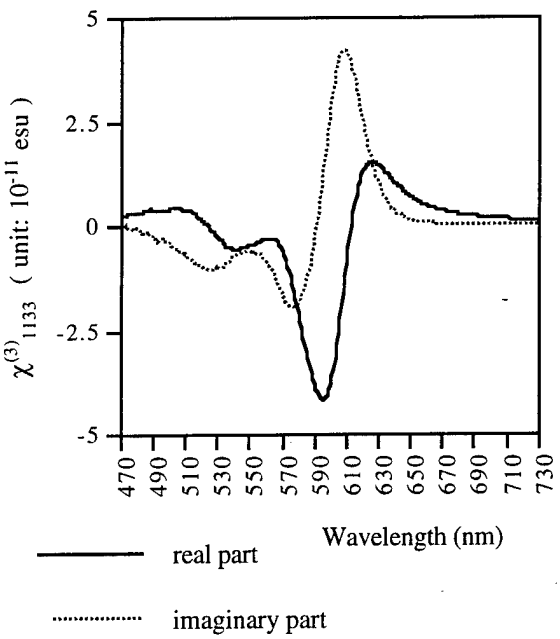

Figure 3. Complex spectrum of $\chi^{(3)}_{1133}$ for poly(BPOD)

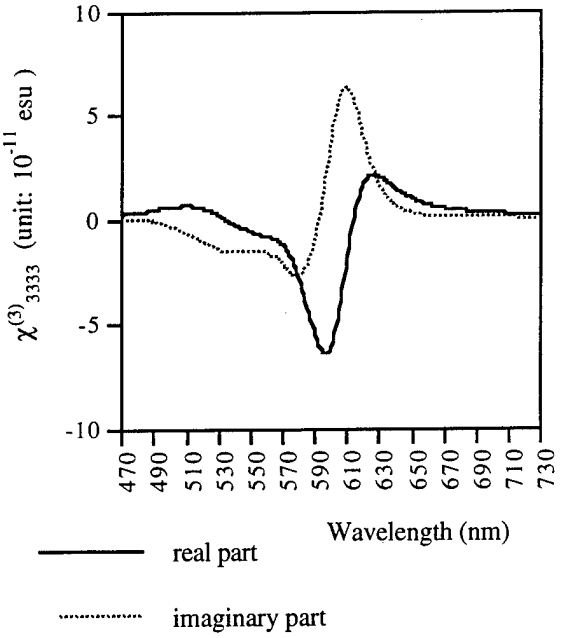

Figure 4. Complex spectrum of $\chi^{(3)}_{3333}$ for poly(BPOD).

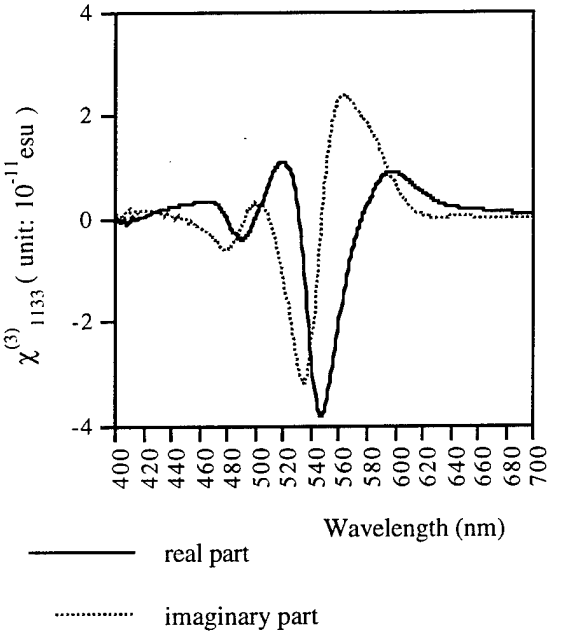

Figure 5. Complex spectrum of $\chi^{(3)}_{1133}$ for poly(4-BCMU).

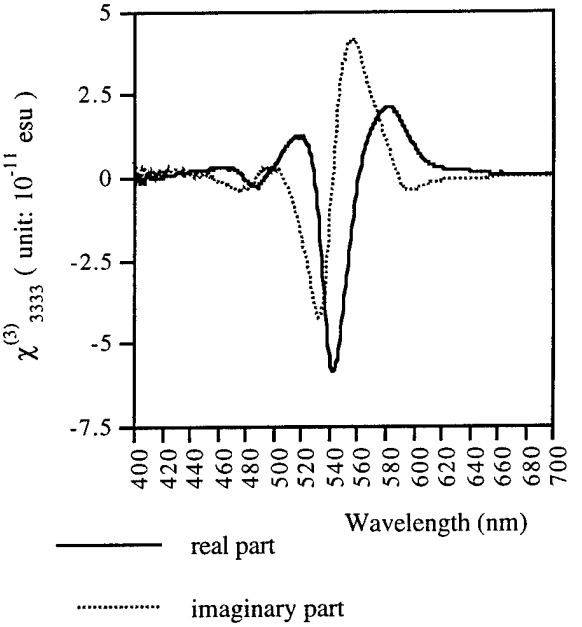

Figure 6. Complex spectrum of $\chi^{(3)}_{3333}$ for poly(4-BCMU).

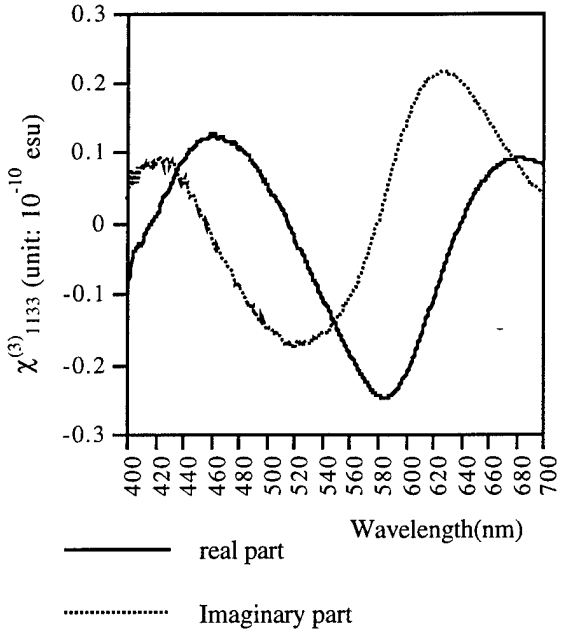

Figure 7. Complex spectrum of $\chi^{(3)}_{1133}$ for BP-2A-NT.

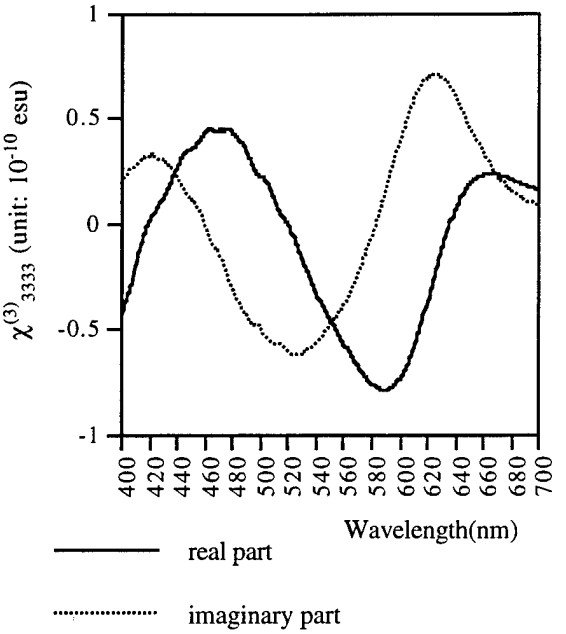

Figure 8. Complex spectrum of $\chi^{(3)}_{3333}$ for BP-2A-NT.

polydiacetylenes) can be treated as one dimensional in shape. It has only one component of microscopic third-order polarizability γ_{zzzz} , where z is along the chromophore direction. We assume the potential energy of the chromophore to be $U = -U_0 \sin\alpha$, where α is the angle between the film normal and the side-chain direction. This potential model represents the interactions among the side chains, main chains and the substrate. The chromophore orientation should satisfy Boltzmann distribution, i.e. the probability of finding a chromophore with angle α to the film normal is proportional to $\exp(-U/kT) = \exp(p\sin\alpha)$, where $p = U_0 / kT$. It can be proved that for one-dimensional chromophore, $\chi^{(3)}_{1133} \propto \frac{\gamma_{zzzz}}{2}\langle\cos^2\alpha\sin^2\alpha\rangle$, and $\chi^{(3)}_{3333} \propto \gamma_{zzzz}\langle\cos^4\alpha\rangle$. Then we have :

$$\frac{\chi^{(3)}_{3333}}{\chi^{(3)}_{1133}} = \frac{2\langle\cos^4\alpha\rangle}{\langle\cos^2\alpha\sin^2\alpha\rangle} = \frac{2\int_0^{\pi}\exp(p\sin\alpha)\cos^4\alpha\sin\alpha\,d\alpha}{\int_0^{\pi}\exp(p\sin\alpha)\cos^2\alpha\sin^3\alpha\,d\alpha} \qquad (6)$$

Computer calculations[8] have shown that when $p < 0$, the ratio of $\chi^{(3)}_{3333}$ to $\chi^{(3)}_{1133}$ is larger than 3, and the chromophores are preferentially oriented normal to the film plane; when p=0, the ratio of $\chi^{(3)}_{3333}$ to $\chi^{(3)}_{1133}$ equals to 3, and the chromophores are distributed isotropically in three-dimensional space; when p>0, the ratio of $\chi^{(3)}_{3333}$ to $\chi^{(3)}_{1133}$ is less than 3, and the chromophores are inclined to lie along the film plane. For poly(BPOD) and poly(BCMU), the ratio of $\chi^{(3)}_{3333}$ to $\chi^{(3)}_{1133}$ is 1.5, significantly less than 3, and we infer that the distribution of the chromophore is lying along the film plane. For BP-2A-NT, the ratio of $\chi^{(3)}_{3333}$ to $\chi^{(3)}_{1133}$ is close to 3, and we infer that the distribution of the chromophore is close to three-dimensional isotropy.

BP-2A-NT also yields appreciable values of $\chi^{(3)}_{1133}$ and $\chi^{(3)}_{3333}$. The maximum value of

$\chi^{(3)}_{3333}$ is even comparable with those of polydiacetelynes. It dose not mean that the chromophore of BP-2A-NT is as strong in third-order nonlinearity as those of polydiacetelynes. The reason is that the polydiacetelyne chromophore (main chain) is inclined to lie along the film plane, and its $\chi^{(3)}_{3333}$ component is significantly reduced by projection from the chromophore orientation to the film normal. While the BP-2A-NT chromophore (side chain) is oriented isotropically in three-dimensional space. This distribution can convert more third-order nonlinearity of the BP-2A-NT chromophore to the $\chi^{(3)}_{3333}$ component. Due to this reason, the epoxy-based nonlinear optical polymer with side-chain NLO chromophore could be a potential candidate for applications involving the $\chi^{(3)}_{3333}$ component. For the same reason, to exploit large value of $\chi^{(3)}_{3333}$ from NLO polymer with main-chain chromophore such as polydiacetelynes, measures to adjust the main-chain distribution should be considered.

Conclusion

Normal and tilted incidence of electroabsorption spectroscopy was used to study the chromophore orientation in NLO polymers, and the information of polymer chain orientation was inferred. The results indicate that the main-chains of the two polydiacetelynes are inclined to lie along the film plane, while the side-chains of the epoxy-based NLO polymer are distributed close to three-dimensional isotropy.

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